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GLASS-CERAMIC COMPOSITE MATERIAL, CERAMIC SUBSTRATE LAMINATE
OR MICROHYBRID HAVING THIS COMPOSITE AND A METHOD FOR
PRODUCING IT

The present invention relates to a glass-ceramic composite material, a ceramic substrate, a ceramic laminate or a microhybrid having this ceramic composite material, as well as a method for producing the composite material or component parts having it, according to the generic parts of the independent claims.

Background Information

Substrate materials for LTCC applications ("low temperature co-fired ceramics") have been developed in the past few years, above all with the aim of reducing the sintering temperature, in order to make possible co-firing, that is, sintering of the entire composite material in one step, with low-melting metals, such as silver. In this context, the compatibility with the metal should be ensured at the same time. It was also an aim to improve the dielectric properties of the LTCC substrate, especially for applications in the high frequency range, and to increase their heat conductivity with regard to heat dissipation from the LTCC substrates.

A glass-aluminum nitride composite material is known from EP 0 499 865 A1, which has a comparatively high heat conductivity at a low sintering temperature, and has good dielectric properties. This composite material starts from a glass powder having silicon dioxide, aluminum oxide, boron oxide and an alkaline earth metal oxide such as MgO, CaO or SrO, to which aluminum nitride is added as a ceramic powder component. Upon

sintering the starting mixture to the composite material according to EP 0 499 865 A1, if MgO is used, cordierite is formed, and if CaO is used, anorthite is formed, while the glass matrix becomes impoverished in silicon, magnesium and aluminum.

It was the object of the present invention to make available a glass-ceramic composite material, especially a substrate material for LTCC applications, which is able to be processed to a ceramic substrate and is able to be used in a ceramic laminate or in a microhybrid, and which has a high overall heat conductivity, if possible in the range of 8 W/mK to 12 W/mK.

Summary of the Invention

The glass-ceramic composite material according to the present invention has the advantage, compared to the related art, that it is very suitable as a substrate material for LTCC substrates and for the construction of microhybrids having such substrates, and that it particularly has a clearly increased heat conductivity, especially in the favorable range of 8 W/mK to 12 W/mK, compared to the usual LTCC substrate materials, whose heat conductivity usually lies between 2 W/mK to 3 W/mK. In this way, the number of required heat dissipations, which are designed in the case of microhybrids, as a rule, as thermal lead-throughs, or so-called "thermal vias", i.e. channels filled with a metal that cross the substrate, may be reduced. Thereby comes about the possibility of clearly reducing the size of such microhybrids and of increasing the layout density.

A ceramic laminate produced using the glass-ceramic composite material according to the present invention, or a microhybrid

based on an LTCC substrate having this glass-ceramic composite material, consequently offers the possibility of saving on thermal vias and of achieving a greater integration density. Finally, silver, that is usually used for filling the thermal
5 vias, will also be saved in part by reducing their numbers.

Advantageous further refinements of the present invention result from the measures indicated in the dependent claims.

10 Thus, it is especially advantageous if the ceramic filler is aluminum nitride having an average powder particle size of 100 nm to 10 μm , especially from 1 μm to 10 μm . In this context, the filler may be uncoated aluminum nitride that has an average particle size such as 1 μm to 3 μm , preferably, coated
15 aluminum nitride having an average particle size such as 6 μm to 7 μm , the coating being preferably a hydrophobic surface modification or an oxygen-containing surface coating. It is particularly advantageous if the aluminum nitride powder used, especially because of the oxygen-containing surface coating,
20 has an oxygen content of 0.5 wt. % to 2.0 wt. %, it being generally accepted that a lower oxygen content leads to an increased heat conductivity of the aluminum nitride-ceramic powder used.

25 In addition it is of advantage if the matrix has as the crystalline phase a Li-Al-Si₂O₃ mixed crystal and/or an Li-Al-Si oxynitride and/or an Li-Al silicate and/or a lithium silicate as the crystalline phase as well as being further made up of a residual glass phase in which nitrogen is soluble
30 at least in small proportions. It is of especial advantage if the matrix contains no lithium silicate, if possible, or as little of it as possible. Furthermore, it is advantageous if B₂O₃ is also put into the starting mixture, so that, at least

from place to place, an Li-B oxide may be created as crystalline phase in the matrix.

The proportion of the ceramic fillers in the composite material is preferably between 25 vol. % and 70 vol. %, especially 30 vol. % to 50 vol. %. It is particularly simple to set a heat conductivity in the range aimed for of 8 W/mK to 12 W/mK via the filler proportion.

10 Brief Description of the Drawing

The invention will be explained in more detail with reference to the drawings and in the description below. Figure 1 shows a top view of a microhybrid having an LTCC substrate as the ceramic substrate.

Exemplary Embodiments

Figure 1 shows a microhybrid 5 known in principle, having a ceramic substrate 10 in the form of an LTCC foil or an LTCC laminate, substrate 10 having, from place to place, thermal lead-throughs 14, so-called "thermal vias", which cross substrate 10 and which are filled with a metal, for example, silver. Furthermore, electrical lead-throughs 11, so-called "electrical vias", that cross the substrate 10, are provided, whereby printed circuit traces running on the upper side of substrate 10 are able to be contacted from the lower side of substrate 10. Finally, on the upper side of substrate 10 there is shown, as an example, a printed-on resistor 13 that is also connected to the printed-on printed circuit traces 12.

The crux of the present invention is to make available a glass-ceramic composite material for producing substrate 10 according to Figure 1.

For this, one first melts a glass from a starting mixture having 20 wt. % to 68 wt. % SiO_2 , 10 wt. % to 25 wt. % Al_2O_3 , 5 wt. % to 25 wt. % Li_2O , 0 wt. % to 33 wt. % B_2O_3 , 0 wt. % to 10 wt. % P_2O_5 , 0 wt. % to 10 wt. % Sb_2O_3 and 0 wt. % to 3 wt. % ZrO_2 .

Preferably, the starting mixture is made up of 48 wt. % to 66 wt. % SiO_2 , 14 wt. % to 22 wt. % Al_2O_3 , 4 wt. % to 20 wt. % Li_2O , 0 wt. % to 20 wt. % B_2O_3 , 0 wt. % to 5 wt. % P_2O_5 , 0 wt. % to 5 wt. % Sb_2O_3 and 0 wt. % to 2 wt. % ZrO_2 .

In the case of the components B_2O_3 , P_2O_5 , Sb_2O_3 and ZrO_2 , these are especially preferably added in a proportion of 3 wt. % to 20 wt. % B_2O_3 and/or 2 wt. % to 5 wt. % P_2O_5 and/or 1 wt. % to 5 wt. % Sb_2O_3 and/or 1 wt. % to 2 wt. % ZrO_2 .

Within the scope of a first exemplary embodiment, the starting mixture is made up of 65 wt. % SiO_2 , 15 wt. % Al_2O_3 and 20 wt. % Li_2O .

Within the scope of a second exemplary embodiment, the starting mixture is made up of 65 wt. % SiO_2 , 15 wt. % Al_2O_3 , 12 wt. % Li_2O and 8 wt. % B_2O_3 .

In a third exemplary embodiment, the starting mixture is made up of 50 wt. % SiO_2 , 16 wt. % Al_2O_3 , 12 wt. % Li_2O and 20 wt. % B_2O_3 .

In a fourth exemplary embodiment, the starting mixture is made up of 65 wt. % SiO_2 , 21 wt. % Al_2O_3 , 4 wt. % Li_2O , 4 wt. % B_2O_3 , 4 wt. % P_2O_5 and 2 wt. % ZrO_2 .

During the production of the glass from this starting mixture, a matrix is created that contains lithium, silicon, aluminum

and oxygen, and which, from place to place, has at least one crystalline phase. This crystalline phase is, for instance, an Li-Al-Si₂O₃ mixed crystal, an Li-Al-Si oxynitride, a lithium silicate or a plurality of such crystalline phases. The non-crystalline regions of the matrix further form a residual glass phase in which, in a small proportion, nitrogen is soluble.

For the production of the above-named glasses, first of all the powder components used in the starting mixture are homogenized and melted at temperatures between 1200° C and 1600° C. After homogenization of the melt, this is then, for example, poured off into water, that is, it is shredded, and the glass thus obtained is milled down to an average grain size of 1 µm to 5 µm, for instance, 3 µm. After that, to this glass powder there is added, as ceramic filler, powdery aluminum nitride, having an average particle size of 100 nm to 10 µm, preferably 1 µm to 10 µm.

Within the scope of a first exemplary embodiment for producing the glass-ceramic composite material from the glass powder and the ceramic filler, one of the previously described glass powders and, as the ceramic filler, aluminum nitride powder, are homogenized in an organic solvent such as isopropanol, the powder mixture thus obtained is first dried, and is subsequently submitted to molding, such a uniaxial pressing.

After that, the pressed element obtained is sintered in air, nitrogen or a gas mixture containing oxygen and/or nitrogen at temperatures of at most 1050° C, so that one obtains thereafter a densely sintered glass-ceramic composite material in which, in a glass-type matrix, which from place to place has crystalline phases, the ceramic aluminum nitride particles are embedded.

On this glass-ceramic composite material, with the aid of the "hot disk method", the heat conductivity was then determined. In this context, it was shown that the latter is a function of the proportion of the added ceramic filler.

Thus, in the case of a glass having 65 wt. % SiO_2 , 15 wt. % Al_2O_3 and 20 wt. % Li_2O in the starting mixture for producing the glass and a proportion of 70 vol. % of this glass and 30 vol. % aluminum nitride particles in the glass-ceramic composite material, a heat conductivity of 9.1 W/mK was determined, and at a proportion of 65 vol. % of this glass and 35 vol. % of the aluminum nitride particles a heat conductivity of 8.9 W/mK was determined, and at 60 vol. % of this glass and 40 % vol. % of the aluminum nitride particles a heat conductivity of 12.5 W/mK was determined.

It has generally been shown that the heat conductivity rises in the glass-ceramic composite material with increasing proportion of aluminum nitride.

The stagnant value of the heat conductivity at a composition of 65 vol. % glass and 35 vol. % aluminum nitride is attributed to the high proportion of crystalline lithium silicate formed. Therefore it is favorable if the glass-ceramic composite material contains as little as possible or no lithium silicate.

Testing for crystalline phases within the matrix of the glass-ceramic composite material and the verification of these phases, by the way, was done by X-ray diffractometry and scanning electron microscopy.

For the production of a ceramic foil, a ceramic laminate or a microhybrid 5 using substrate 10 made of the above-described glass-ceramic composite material, there is first produced one of the glasses described, it is ground down to the grain size described, and mixed with the described ceramic filler aluminum nitride. Thereafter, there is added to the powder mixture preferably additional, known per se components such as a solvent, an organic binding agent, as well as preferably also a dispersing agent, and then one carries out the forming of the mixture, especially to a foil, a layer or a laminate. After forming, first, preferably the binder is removed, and then the foil, layer or laminate is sintered at at most 1050° C in air, nitrogen or a gas mixture containing oxygen and/or nitrogen. In this way, the added binder and the solvent as well as the dispersing agent are at least to a great extent removed again by pyrolysis, so as to create a glass-ceramic-composite material in the desired shape that is free from these temporary components. On the exemplary foil thus produced, which is used as substrate 10 for microhybrid 5, the latter is then constructed in the usual manner for this design layout technology.